



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title:
“ Structure of promoters and aluminium in Raney-type nickel catalysts ”

Experiment number:
HS-3612

Beamline:
ID31

Date of experiment:
from: 01 March 2008 to: 03 March 2008

Date of report:
-- ----- 2008

Shifts:
6

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Report:

Aim of the experiment and scientific background

One of the objectives of the IMPRESS Integrated Project [1] is to develop more efficient and cheaper nickel catalyst powders, so called Raney-type nickel catalysts. These catalysts are widely used for hydrogenation reactions in industry. They are generally prepared from very finely divided Ni-Al 50-50 wt% alloys. Traditional research in this area focuses on the production of such powders by casting-and-crushing and subsequent leaching with NaOH solution to remove most of the aluminium in order to activate the catalyst [2]. In the case of Raney-type Ni catalysts, mainly metallic Ni nanoparticles with a very large surface area remain after the leaching process.

Until now the structure and microstructure of leached powders is not well known. The powder catalyst is mainly metallic nickel but some metallic aluminium remains at the near surface. The remaining aluminium could play an important role in the relationship between catalytic performance and microstructure. It is thus of great importance to know what is the structure and the composition of this aluminium at the near surface of Raney-type nickel catalysts.

Adding a low amount (around 2 wt %) of a third metal (Cr, Ti, Mo...) as promoter is common to increase the catalytic performance of Raney-type nickel catalysts. The promoting effect can be on activity but also on selectivity towards one desired product which is of great industrial interest. XPS analysis shows that remaining aluminium and promoters are present in a significant amount at the near-surface. The relatively low amount of bulk aluminium (and also of promoters in case of doped material) is impossible to detect with conventional laboratory equipment. As Raney-type nickel catalysts consists of agglomerates of small particles (5-8 nm), transmission electron microscopy study is of little use.

High resolution XRD is essential to study the structure of the remaining aluminium and promoters of Raney-type nickel catalysts, as well as to provide further information on the characteristic of the Ni formed during the leaching process.

Nb. This experiment forms part of a general work-plan for the IMPRESS Integrated Project, as stated in a Memorandum of Understanding between ESRF, ILL and ESA in December 2006.

Experimental details

Ni-Al powders of selected composition and size, before and after leaching, were put into capillaries of 0.6 mm of inner diameter. Raney-type powders are highly pyrophoric and were encapsulated wet in order to avoid oxidation in contact with air. Powder diffraction patterns were recorded with a wavelength $\lambda = 0.39996710 \text{ \AA}$ and an exposure time of approximately two hours in order to get a sufficient statistic and identify the phases present even in small amount. 17 powders in total were measured during the allocated time.

Results

Non-leached powders :

The diffraction patterns of non-leached powders with a grain diameter in the range 53-150 μm displayed the characteristic peaks of the Ni_2Al_3 , NiAl_3 and Al compounds. No other phases were detected in the powders containing the Cr promoter. Rietveld refinement of the diffractograms (Figure 1a) enabled a quantitative evaluation of the phase fraction. The results are in agreement with previous analysis using neutron diffraction [3].

Several diffraction patterns of non-leached powders with a grain diameter $< 38 \mu\text{m}$ displayed small peaks which could not be investigated in previous study to due an overlapping with the reflections of others phase. The high angular resolution available on ID31 enabled to separate and identify some of them (figure 1b). The characteristic peaks of the metastable decagonal quasicrystal D-AlNi observed by C.Pohla and P.L. Ryder in splat-cooled Ni-Al alloys [4] were identified. Further investigations of the smaller non-identified peaks are being performed by comparing their positions with the ones expected for other metastable phases encountered in the Ni-Al system such as Ni_2Al_9 .

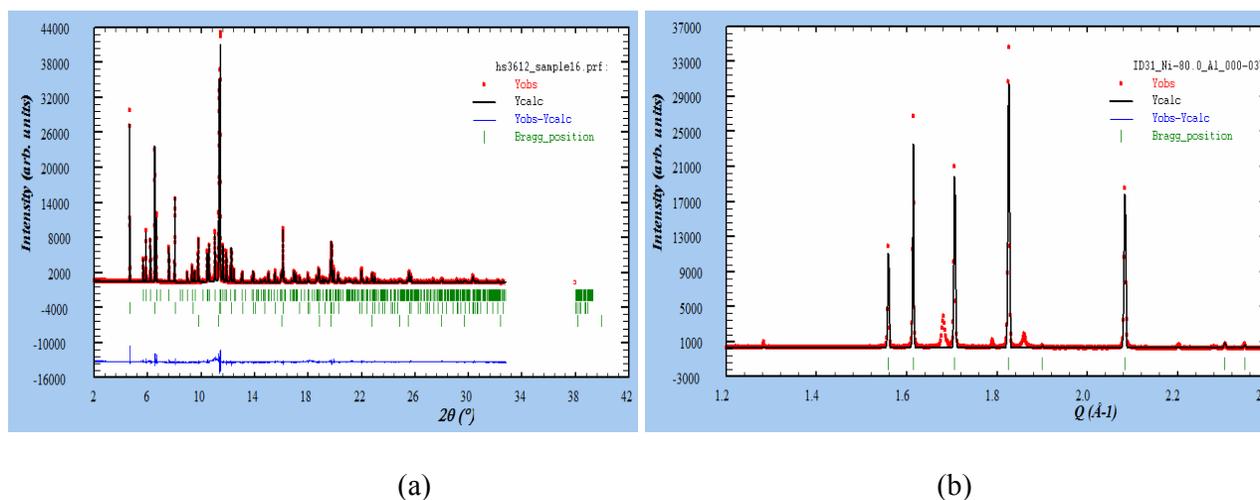
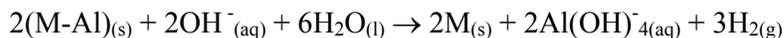


Figure 1, (a) Refined diffraction pattern of a Ni-75at%Al non-leached powders with a grain size 75-106 μm and (b) partial diffraction pattern showing peaks of unidentified phases in Ni-80at%Al non-leached powders with a grain size $< 38 \mu\text{m}$.

Leached powders :

A typical diffraction pattern obtained from a leached powder is shown figure 2a. Large peaks corresponding to Raney-nickel are visible. Scattering at small angle which is characteristic of the Raney-nickel structure is also present. The pronounced lorentzian shape of those peaks suggest a strong influence of the sample on the diffraction pattern implying very small cristallites. One can also notice the occurrence of sharp peaks. The latters were in most cases identified as belonging to bayerite $\text{Al}(\text{OH})_3$ as shown figure 2b. Bayerite is a by-product of the leaching reaction which can be written :



Precipitation of $\text{Al}(\text{OH})_3$ is mainly prevented by performing the leaching of powders using a solution with an excess of sodium hydroxide and washing the leached powders several times with demineralised water before storage. It is then unexpected to detect this compound which was not mentionned in previous studies performed with less precise angular resolutions. However, bayerite peaks were found less pronounced in the case of powders leached on site only one week before the experiment. It is then suggested that bayerite formed during the storage of the powders. Furthermore, additional small sharp peaks of compounds which are not yet determined were observed in several samples. The latter observation emphasises the possible formation of compounds with time during storage. Their respective influence on the catalyst activity remains to determine.

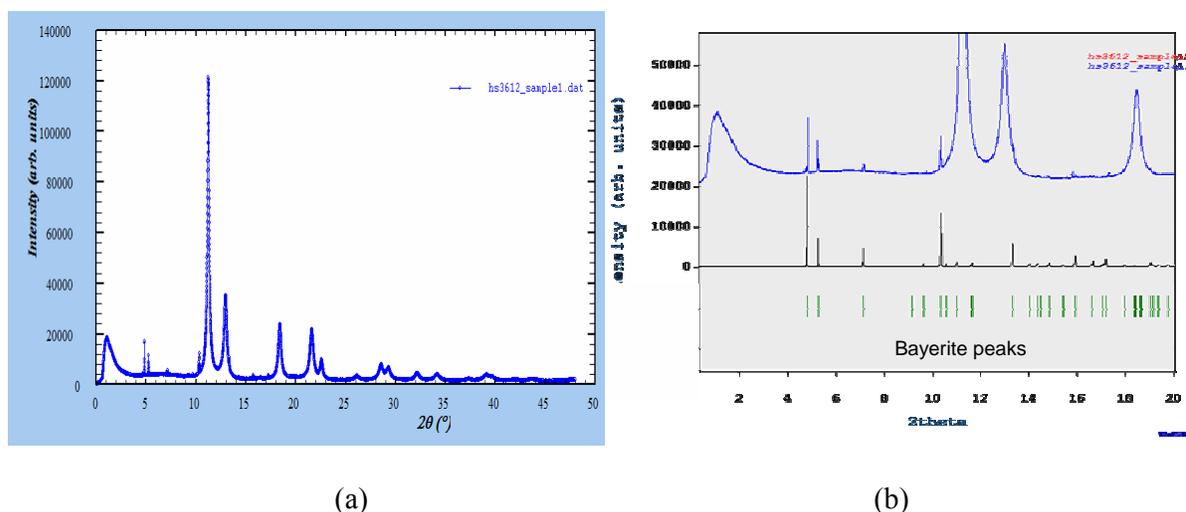


Figure 2, (a) Diffraction pattern of a leached Ni-77.5at%Al powder with a grain size 106-150 μm and (b) zoom including the positions of calculated bayerite peaks.

The influence of the addition of Cr-dopent on the pattern of leached powders is shown figure 3. Additional bayerite peaks previously mentionned are visible in the diffraction pattern of the non-doped powder as well as Raney-Ni peaks. Ni_2Al_3 is also detected in the doped powder and Raney-Ni are broader. It can then be concluded that the leaching process is less efficient on the Ni_2Al_3 phase and that Ni particles which formed are smaller when Cr is added to the precursor. No compounds containing Cr are detected. This suggest that a solid solution is formed with Cr atoms incorporated in the Ni or Ni_2Al_3 lattices.

Finally figure 4 displays the diffraction patterns after leaching of Ti-doped powders. Sharp and intense Ni_2Al_3 and bayerite peaks appears with smaller broad peaks of Raney-Ni, still accompanied by scattering at small angle. No Al_3Ti peaks are detected whereas this intermetallic compound has been identified in the intial atomised powders [3]. Like Cr, Ti could remains in the form of a solid solution. Preliminary Rietveld refinements were performed in order to determine if variations of the lattice parameters of Ni_2Al_3 and Raney-Ni corroborate that assumption and no clear evidence were noticed. Further work are in progress to improve modelisation of the peak shape of the leached powders in order to provide quantitative measurements.

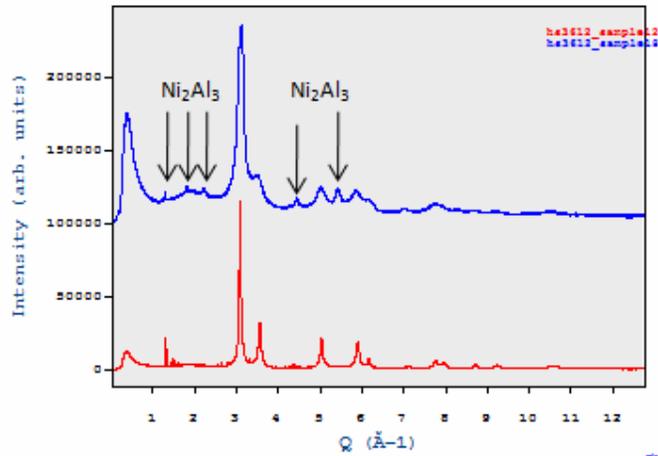


Figure 3, Diffraction patterns of a leached Ni-75at%Al powder with a grain size 106-150 μm . Bottom graph, without Cr, up graph Cr-doped.

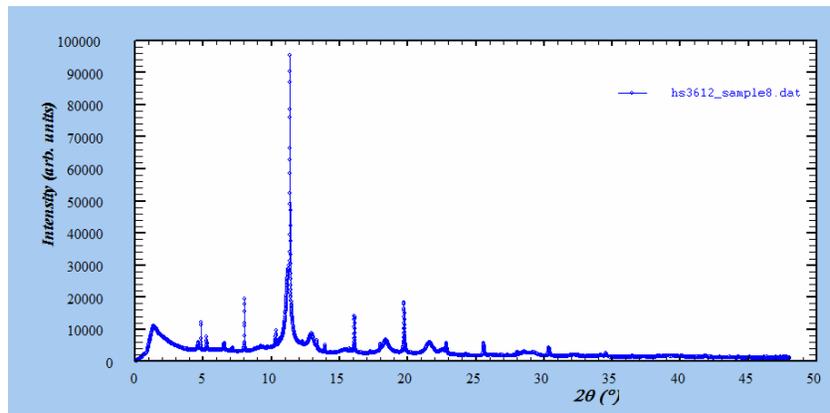


Figure 4, Diffraction patterns of a leached Ti-doped Ni-68.5at%Al powder.

- [1] D.J. Jarvis and D. Voss, *Materials Science and Engineering: A*, 413-414 (2005) 583.
- [2] F. Devred, B.W. Hoffer, A.D. van Langeveld, P.J. Kooyman and H.W. Zandbergen. *Appl. Catal. A*. 244 (2003) 291.
- [3] U. Dahlborg, C. Bao and M. Calvo-Dahlborg, *Groupe de Physique des Matériaux, Uni Rouen* 2006.
- [4] C. Pohla and P.L. Ryder,